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ScienceDirect
Energy Procedia 63 (2014) 4575 – 4584
Energy Procedia

GHGT-12

Preliminary Feasibility Study for On-Site Hydrogen Station with Distributed CO_2 Capture and Storage System

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Abstract

It is important to produce Carbon-Free Hydrogen for FCV. Current Japanese situation, it is difficult to fully supply the Carbon Free Hydrogen is generated by water-electrolysis (WE_R) using renewable energy. This study presents the Steam reforming for natural gas ($_N$SR) with decentralized CCS system for producing Carbon-Free Hydrogen. The CCS cost is covered by the differential cost between WE_R and $_N$SR Hydrogen production cost. Our preliminary investigation suggests the differential cost between WE_R and $_N$SR Hydrogen enough to cover the cost of decentralized CCS (under 1000 ton-CO_2/y). We also analyze the feasibility of Mother-Daughter type of Hydrogen supplement system with decentralized CCS. In this case, $_N$SR with CCS system has advantage against WE_R Hydrogen production systems. These investigations clearly indicate the high potential of $_N$SR with CCS system but it is carefully discussion about CO_2 behavior in the reservoir by well-established and newly developing methods for safety.

Peer-review under responsibility of the Organizing Committee of GHGT-12

Keywords: Carbon free Hydrogen; FCV; Decentralized CCS; PAMAM membranes;

1. Introduction

Widespread of Fuel cell vehicles (FCV) is one of essential solutions to mitigate the emission of carbon dioxide (CO_2) and the introduction to a market is scheduled in 2015 in Japan. FCV uses hydrogen fuel, which can be produced from various sources. And carbon-free hydrogen for FCV is strongly required. Generally Carbon-free

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Peer-review under responsibility of the Organizing Committee of GHGT-12
doi:10.1016/j.egypro.2014.11.490

hydrogen is produced by water-electrolysis (WE_R) method with renewable energies such as solar power or wind power, though such energies are not still popular and are high-cost in Japan.

It is considered that petroleum refining factory and steam reforming of natural gas ($_NSR$) equipment are promising alternative processes for hydrogen production until establishing renewable energy community in Japan. However, hydrocarbon-originated hydrogen is not "carbon-free hydrogen" at this moment, since CO_2 is also generated as a by-product. Hydrogen production by $_NSR$ with CCS is reasonable way to produce carbon-free hydrogen from the hydrocarbon in Japan next several decades.

In Japan, large-scale CO_2 reservoirs (over 1Mt/year) for CCS are very limited because of complicated geological situation. However, the small to medium scale reservoirs are estimated to exist abundantly even in Japan. Kashiwagi et al. [1] estimated the storage potential of shallower level of aquifer less than 750 m in depth is around 33.6 Gt-CO_2. Other groups also reported the feasibility of shallower reservoirs for CCS [2]. Based on these reports, the potential of small to medium scale CCS in Japan is sufficiently high and it contributes to mitigate CO_2 emission by the utilization of these reservoirs for small-scale CCS (~100 thousand ton/y) with newly developed concept and technologies for CO_2 capture, storage and monitoring method.

In this study, we discuss the feasibility of production of carbon-free hydrogen from $_NSR$ method combined with small-scale CCS system, "Decentralized CCS".

2. Costs of carbon-free hydrogen

In this study, we focus on an on-site hydrogen station for FCV. This station is equipped with both system of $_NSR$ system to produce hydrogen from natural gas and CCS. There are well-established natural-gas supply systems (pipe line), and thus, this is considered to be a feasible model in everywhere Japan. First, we compared the hydrogen production costs between WE_R-hydrogen and $_NSR$ -hydrogen by taking into account of Japanese energy conditions. First, we assumed that the costs of hydrogen production in both equipments are almost same and that the electricity in WE_R and the source gas in $_NSR$ are renewable energy and natural gas (NG), respectively. Table 1 shows unit price (USD) of carbon-free renewable electricity in Japan.

Source type	Unit Price (USD/kWh)
Solar Energy	0.32
Wind power	0.22
Geothermal Energy	0.26
Small scale Hydropower	0.21
Average	0.25

Table 1 Unit Cost of Renewable Energy in Japan

These electricity costs are based on the buying price by Japanese government. We employed the average unit price (0.25 USD/kWh) of these sources as the electricity cost in WS-hydrogen production The unit price of natural gas for $_NSR$ -hydrogen is used an averaged unit prices of four Japanese major gas companies as 0.99USD/Nm^3-NG.

Table 2 summarizes the result of the cost estimation in WE_R-hydrogen and $_NSR$ -hydrogen production. These results indicate that the hydrogen price of $_NSR$ -hydrogen is cheaper than that of WE_R-hydrogen in Japan. The cost difference between WE_R-hydrogen and $_NSR$ -hydrogen is 0.90USD/Nm^3-H_2 and is used for small scale CCS.

Next, we estimate the annual volume of produced hydrogen and CO_2 at one $_NSR$ -hydrogen production station, based on the following two assumptions. (1) This station has a hydrogen supply capacity of 300Nm^3-H_2/h [3]. (2) CO_2 is separated from PSA off-gas and subsequent pressure swing adsorption with high-recovery rate. (3) Operation time is 12h/day, 350day/year and 30years. In this case, the total volume of the produced hydrogen and CO_2 by-product are 1260000 Nm^3-H_2/year and 1013.4 ton-CO_2/year, respectively. In our model, the recovery ratio of CO2 is set 95% and the volume of captured CO_2 is 962.7 ton-CO_2/year. From these estimations, total injected CO_2 volume is calculated to be 28881 ton-CO_2.

In next section, we discuss the reasonable and acceptable decentralized CCS model for 28881 ton CO_2 under 0.90

millions USD for total cost.

	WE_R Hydrogen	$_NSR$ Hydrogen
Production rate for Hydrogen	*5.03 kWh/Nm^3-H_2	*0.36 Nm^3-NG/Nm^3-H_2
Energy Source	Renewable energy	Natural Gas
Unit Price	#0.25 USD/kWh	+0.99 USD/Nm^3-NG
Hydrogen price	1.26 USD/Nm^3-H_2	0.36 USD/Nm^3-H_2
Carbon free	Yes	No, Requirement of CCS

*Private communications; #METI website [3]; +JHFC report, [4]

Table 2 . Production costs for WE_R and $_NSR$ Hydrogen

3. Discussion for acceptable and reasonable models of decentralized CCS

Generally, it is considered that it is a conflict relationship between safety and economy in CCS. We have to search reasonable and consistent model to produce the carbon-free hydrogen by on-site hydrogen station with decentralized CCS model as safety and economy. Our model clearly indicates that user of FCV are both of beneficiary person and burden person. We have to establish acceptable model for present and future users of FCV. Previous study reported the target cost of large scale CCS as follow; capture is 0.083 USD/m3-CO_2, Transportation is 0.016 USD/m3-CO_2 and storage is 0.045 USD/m3-CO_2. In this study we discuss the cost of CCS based on these value and investigate the feasibility of on-site $_NSR$ -hydrogen station with decentralized CCS.

3-1 CO_2 capture by PAMAM membranes

Previous study indicated that part of CO_2 capture is the costliest part for large scale CCS. Their model is using absorbent to capture CO_2. Because, absorbent is high cost itself and they need large energy for release CO2. As a first step, we discuss the potential of cost reduction about CO_2 capture technology. In this study, we adopt polymeric membrane separation method to reduced CO_2 capture cost and energy.

Poly (amidoamine) (PAMAM) dendrimers are promising materials in CO_2 separation over N_2 in a liquid immobilized membrane system [4]. A PAMAM-containing polymeric membranes exhibit excellent CO_2 separation properties over H_2 [5]. For example, the CO_2 selectivity and permeability are 230 and 3.7×10^{-15} m^3(STP)/(m^2 s Pa) (or 0.99 GPU), respectively at 42 kPa of CO_2 partial pressure and 298 K, which is close to the pressure of CO_2 in the PSA off-gas in H_2 purification by PSA manner.

PAMAM-containing membranes would be effective and suitable to capture CO_2 in the PSA off-gas due to the high separation performance as shown in Fig.1. The PSA off-gas consists of mostly H_2 (27.5 %) and CO_2 (50.4 %) at ambient temperature and pressure. When the CO_2 is captured, the combustion efficiency of the resulting off-gas is increased and CO_2 emission is considerably suppressed. As a result, CO_2-free H_2 is available.

Cost increase is then calculated by adding the CO_2 capture with PAMAM-containing membranes. Here, CO_2 recovery is 95 %, which is equivalent to required CO_2 recovery in pre-combustion CO_2 capture with polymeric membranes [6]. First, H_2 production at a H_2 station is assumed to be 300 Nm^3/h. In the H_2 purification by PSA, the PSA off-gas is emitted with 180 Nm^3/h, where CO_2 and H_2 fluxes are 90 and 50 Nm^3/h, respectively. With the CO_2 separation properties above mentioned, the required membrane area, A, is determined to 172 m^2 by the following equation.

$$A = CO_2 \text{ flux} \times \text{recovery}/P(CO_2) \times p(CO_2), \qquad \text{eq.1}$$

Where $P(CO_2)$ and $p(CO_2)$ are CO_2 permeability (GPU) and CO_2 partial pressure (kPa), respectively. $P(H_2)$ of the PAMAM-containing membrane is 3.2×10^{-14} m^3(STP)/(m^2 s Pa) (or 4.3×10^{-3} GPU) under the operation conditions,

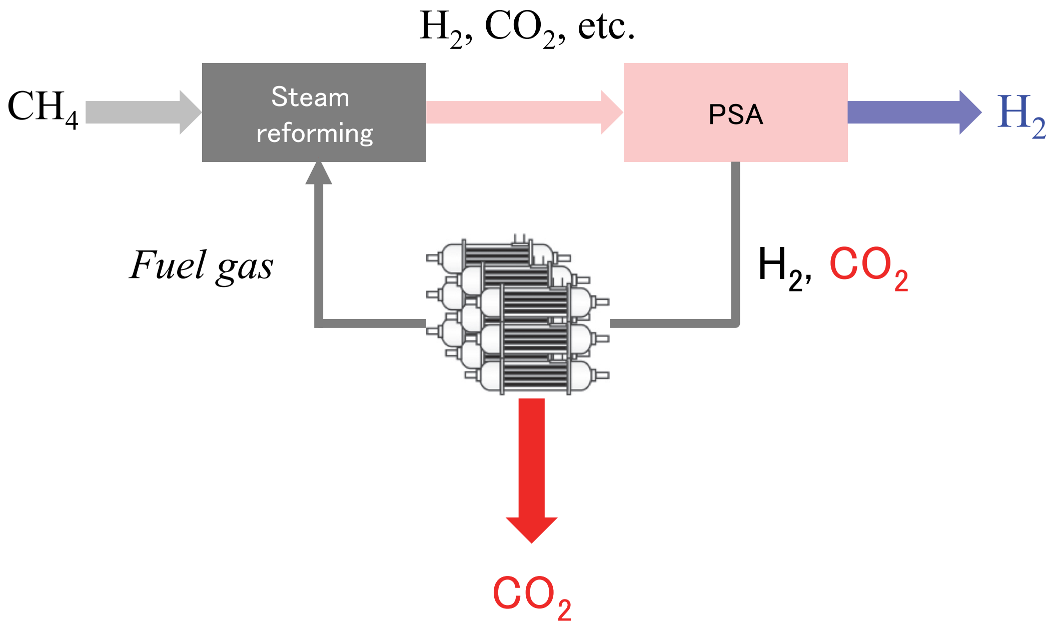

Fig. 1. Schematic diagram of CO_2 capture by PAMAM-containing membrane in H_2 production.

and the H_2 flux in the permeate is 0.15 Nm^3/h. Thus, the CO_2 purity in the permeate can be determined to 99.9 %.

When the unit cost of a membrane is set to 200 USD/m^2, the total membrane cost is 34,000 USD. With a 5,100 USD module cost, fabrication of the membrane module requires 39,100 USD. In a H_2 station, working conditions of the membrane module is set to be 12h/d and 350 day/year, and the operation period is 5 years. In this case, 7.2×10^{-3} USD /Nm^3-H_2 is calculated for the CO_2 capture. This cost simulation tells that the CO_2 capture cost by PAMAM-containing membrane is quite promising. In membrane separation, difference in the partial pressure or chemical potential between feed and permeate side drives the separation. Thus membrane separation doesn't require any additional energy in comparison to the current CO_2 capture technology, such as liquid amine scrubbing.

Above mentioned reasons, we are sure that the potential of polymeric membrane separation method is most reasonable separation method for this model.

3-2 Cost of CO_2 storage and the monitoring of CO_2 behaviour in reservoir

CO_2 storage cost is strongly depended on a geological characteristic of CO_2 injection site. Hydrological and physical properties of geological formation (e.g., CO_2 injectivity) are much different for CO_2 injection site.

In this study, we assume an ideal geological formation of injecting-site is late-Pliocene shelf to hemipelagic marine sediments and has good lateral continuity around 2km. This model site has two saline-aquifers for the candidate of CO_2 reservoir at 500m and 800m in depth. Both aquifers have enough thickness and are overlaid thick hemipelagic mudstone. Thickness of both aquifers is set as 30m. The porosity is set as 30%. There are frequent minor sand layers and mud layers between both saline aquifers at 500m and 800m depth. There are frequent minor sand and mud layers above of 500 m aquifer too. Aquifer of 800m overlay Neogene basement rock. Formation water of 500m-depth does not have connection with shallower drinking water (<300 m).

Both of analyses incorporate similar CO_2 monitoring system with three monitoring-wells. These monitoring systems are composed of permanent microtremors monitoring system, permanent pH and pCO_2 monitoring sensors for formation water and pressure sensors of four well-heads. In this model, furthermore, we plan to conduct reflection seismic survey and well logging at every wells in every two years, and quality surveys for drinking and surface water of surrounding area of injection site. It is also included in monitoring cost. For the basement survey cost, we include seismic reflection and array analysis of microtremors.

First, we estimate the CO_2 storage cost of basic cases, which a just under SR-hydrogen production station has one injection site just under hydrogen station (1 on 1 model). We analyze two cases, which use different depth level of aquifers for CO_2-reservoir (Table3).

Basic case: 1 on 1 model

Number of Hydrogen station	1
Total injected CO_2 Volume (t)	28881
Reservoir	
Depth (m)	500 & 800
Thickness (m)	30
Lithology	Sandstone
Porosity (%)	30

Table 3. Model setting for Basic Case

The operation time of the hydrogen station is set as 12h and 350day. Recovered CO_2 at the station is immediately injected into reservoir. We have to suspend CO_2 injection 15 days in every year for safety check for station and well equipment and well-logging operation.

The injected CO_2 volume is 962.7 t-CO_2/y based on JHFC hydrogen production model and operation time is set as 30 years and total injected CO_2 volume reaches 28881 ton.

Results of these estimations are Table 4. Both cases indicate low cost, which is included differential hydrogen cost between natural gas reforming and renewable energy. We also estimate the necessary space for both cases. CO_2 distribution is assumed a disc-shaped and distribution diameter *R* is evaluated by using following estimation method (eq.2), which is arranged equation based on [7].

$$R = \sqrt{\frac{V_{total}}{\alpha \times \pi \times d \times \varphi}} \qquad \text{eq.2}$$

where, V_{total} is total injected-CO_2 volume (Nm^3-CO_2), d is the thickness of the reservoir (m) and ϕ is porosity (%). The α is calculated from CO_2 saturation, CO_2 density and pore utilization ratio [7]. In this study, pore utilization ratio is set as 0.5.

Depth (m)	Total CCS cost (USD/Nm^3-CO_2)	Predicted CO_2 distribution-radius (m)
500	0.410	126.14
800	0.535	52.77

Table 4. Results of cost analyses for 1 on 1 model

This comparison indicates meaningful results. In the both of cases, the total costs of CCS (capture and storage cost) indicate that the cost (0.404 and 0.529 USD for 500 m and 800 m in depth) for CCS operation at the $_N$SR - hydrogen site is sufficiently low. Based on the costs for CCS without the running costs, we can produce carbon-free hydrogen as 0.764 and 0.889USD/Nm^3-H_2 for 500 m and 800 m in depth, respectively. These production costs are 44% and 35% lower than that of WE_R-hydrogen in Japan. Form these estimations, it is concluded that the $_N$SR -hydrogen production with decentralized CCS system is feasible to produce the carbon-free hydrogen even in current Japanese economical and social conditions.

Table 4 also indicates the area of the injected CO_2 distribution (diameter) at the depth of 500 m and 800 m. In the case of shallower reservoir, the state of CO_2 is in gaseous-phase resulting in extreme large diameter over 100m in a radius. This result may be unacceptable to obtain the public acceptance (PA) and permission at town-area, though it may be allowed at the farm area in Japan. On the other hands, CO_2 become super-critical phase in a deeper reservoir (800m) and it total volume is reduced to 57.43 m in a radius. This smaller footprint has much high potential to receive PA and permission even at town area. However, the result of cost analysis with the basic model indicated that the use of a deeper reservoir requires higher cost compared to the shallower model (about 13 % increase).

It is also necessary to consider the case of the hydrogen station without a suitable CO_2 reservoir near or under the station, since there may not be suitable geological formations for CO_2 storage near the station. This scenario is important to propose the $_N$SR-hydrogen station with CCS based on mother-daughter system, which contains one H_2 production site and few supply stations.

4. Investigations for feasibility of the on-site $_N$SR -hydrogen station with decentralized CCS

The place of the hydrogen station, which is demanded, is sometimes different from that of CCS by considering geological situation. This situation is easily supposable and should be considered to develop $_N$SR -hydrogen station with decentralized CCS system. For this purpose, we analysed two types of "mother-daughter" system for supplying hydrogen with CCS systems.

The first system is a "CO_2 transportation system" (CT system), which is composed, of several on-site hydrogen stations and one CO_2 injected site. Captured-CO_2 is transferred to the CO_2-injection site by the trailer with CO_2 liquid tank. Each hydrogen station has a tank to stock the liquid of recovered CO_2. Each hydrogen-production equipment and the total volume of recovered CO_2 are same as the corresponding values in a basic-case, 300Nm^3-H_2/h and 962.7 ton-CO_2/y, respectively. The reservoir is also identical to the model of basic-case.

We analysed the four different cases, transportation of recovered CO_2 from different numbers of $_N$SR -hydrogen production station to one CO_2 injection site, to estimate the total costs (Table 5). In each cases, the total volumes of injected CO_2 from the stations are as 57762 ton, 86643 ton, 115524 ton and 144405ton, respectively.

Hydrogen Production Station number (St.)	2	3	4	5
*CO_2 storage cost (USD/Nm^3-H_2)				
500m	0.201	0.134	0.100	0.081
800m	0.264	0.176	0.132	0.106
*CO_2 Capture cost (USD/Nm^3-H_2)	0.007	0.007	0.007	0.007
+CO_2 transferred cost (USD/Nm^3-H_2)	0.368	0.368	0.368	0.368
Total cost (USD/Nm^3-H_2)				
500m	0.576	0.509	0.475	0.456
800m	0.639	0.551	0.507	0.481

* This study, + Calculated value based on JHFC report [4]

Table 5. Production costs for WE_R and $_N$SR Hydrogen in Mother-Daughter model with CO_2 transportation system

In all cases, the total costs are low compared to 0.90 USD/Nm^3-H_2, which is the cost difference between the systems of WE_R-hydrogen and $_N$SR -hydrogen. We find the volume effect over 3 stations in shallower reservoir case (Fig.2). The total cost of decentralized CCS reduces with increasing $_N$SR -hydrogen production station. The total cost of 5 stations is 20% lower than that of 2 stations case with 500m-reservoir model. In the 800m-reservoir model, this cost reduction reaches 25%. However, CO_2 transportation is extreme high compare to storage cost and all CT system indicate higher cost than 1 on 1 model.

Second mother-daughter system is a “hydrogen transportation system” (HT system). In this estimation, we use the reported cost for hydrogen transportation (0.216 USD/Nm^3-H_2) [9]. This case has a cost advantage against CT system. For example, the HT system with four hydrogen supply station has the cost advantage of 0.02 USD/Nm^3-H_2. This value is calculated by considering the number of hydrogen-production equipments from CT system to HT system. In this case, required hydrogen volume is 151200000 Nm^3-H_2 by two hydrogen-production equipments (operation time 24hours and 350 days). In this case, this HT system reduces the number of hydrogen production equipment from four to two compared with the same hydrogen production scale of CT system. The unit cost of this equipment is about 1.5million USD and hydrogen transportation system has the advantage of 3 million USD of against same scale of CT systems.

Hydrogen-supply station number (St.)	2	3	4	5
CO_2 storage cost (USD/Nm^3-H_2)				
500m	0.201	0.134	0.100	0.081
800m	0.264	0.176	0.132	0.106
CO_2 Capture cost (USD/Nm^3-H_2)	0.007	0.007	0.007	0.007
H_2 transferred cost (USD/Nm^3-H_2)	0.216	0.216	0.216	0.216
Cost advantage (USD/Nm^3-H_2)	-0.020	-0.013	-0.020	-0.018
Total cost (USD/Nm^3-H_2)				
500m	0.404	0.344	0.303	0.286
800m	0.467	0.386	0.335	0.311

* This study, + NEDO report [4]

Table 6. Production costs for WE_R and $_N$SR Hydrogen in Mother-Daughter model with H_2 transportation system

Table 6 shows the estimation results of this HT system in case of 2, 3, 4 and 5 hydrogen-supply stations models. The results of cost analyses for HT system suggest the volume effect on total CCS cost (Fig.2). All cases estimate the lower cost than the 1 on 1 model. These also estimations strongly indicate that each HT systems have large cost advantage against CT systems. In our estimation, cost advantages of HT systems reach 27-37 %. The volume effect is also confirmed in this case and they are around 30 and 42 % in case of 5 hydrogen supply system. From these analyses, the $_N$SR -hydrogen production with decentralized CCS concept with hydrogen transportation type of mother-daughter system is sufficiently reasonable method to product carbon-free hydrogen in Japan.

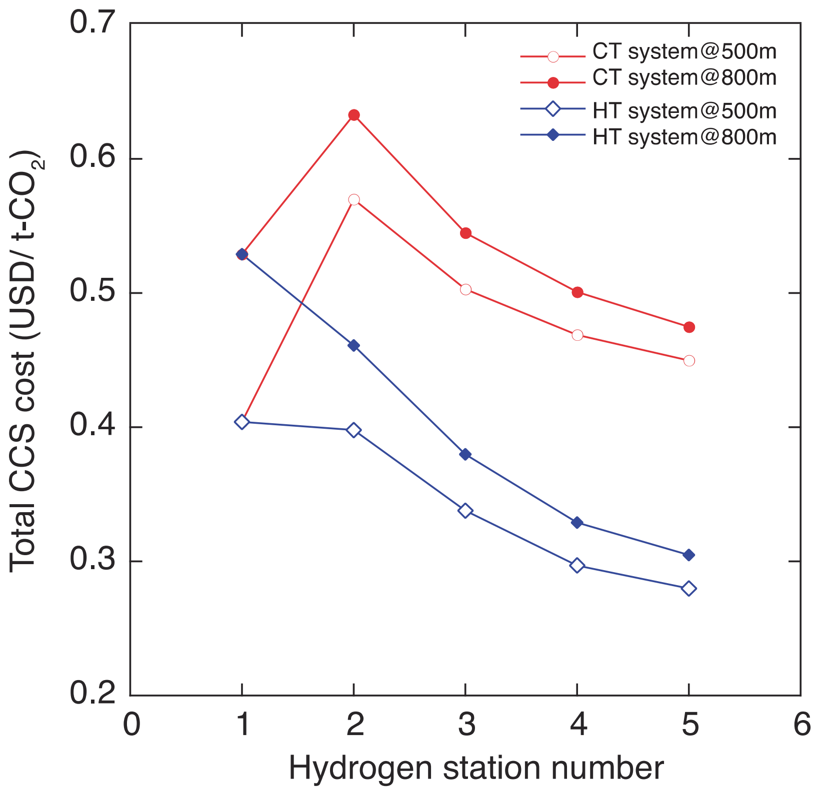

Fig. 2. Comparison with Hydrogen station number and total CCS

We also estimate the CO_2 distribution size for the 1on1 model and all Mother-Daughter system by using eq. 2. The estimation results are listed in Table 7.

Hydrogen Station no.	1	2	3	4	5
Total injected Volume (t-CO_2)	28881	57762	86643	115524	144405
Distribution radius size (m)					
Depth 500m	126.14	178.39	218.48	252.28	282.06
800m	52.77	74.62	91.40	105.53	117.99

Table 7. Relationship between total injected CO_2 volume and size of CO_2 distribution

These results indicate relatively large CO_2 distribution size from 50 m to 300 m. This distribution size may be not suitable near or in town regions. We have to carefully analyze and discuss the acceptable CO_2 distribution size in Japanese land use.

5. Conclusion

We analyze and investigate the most stable on-site $_{N}$SR -Hydrogen station with decentralized CCS model based on economical simulation and simple reservoir models with newly developed CO_2 separation and capture technique. Our cost analysis confirms the extreme high potential of PAMAM membranes. We adopt this separation method and succeed the capture and separation cost cut over 92 % for previous method. Our cost analyses indicate that even simple 1 on 1 model reaches lower cost compared to the cost difference between WE_R Hydrogen and $_NSR$ Hydrogen (0.9 USD/ Nm^3-H_2) in current Japanese energy situation. However, there are a lot of limitation to use saline aquifer for CCS by Japanese geological situation and land use situation restriction.

We investigate the potential of Mature-Daughter hydrogen supply system. From our investigation results, it is clear that Hydrogen transportation type of Mather-Daughter system have large potential to product Carbon-free Hydrogen by $_NSR$ -Hydrogen process combined with decentralized CCS (Fig.3).

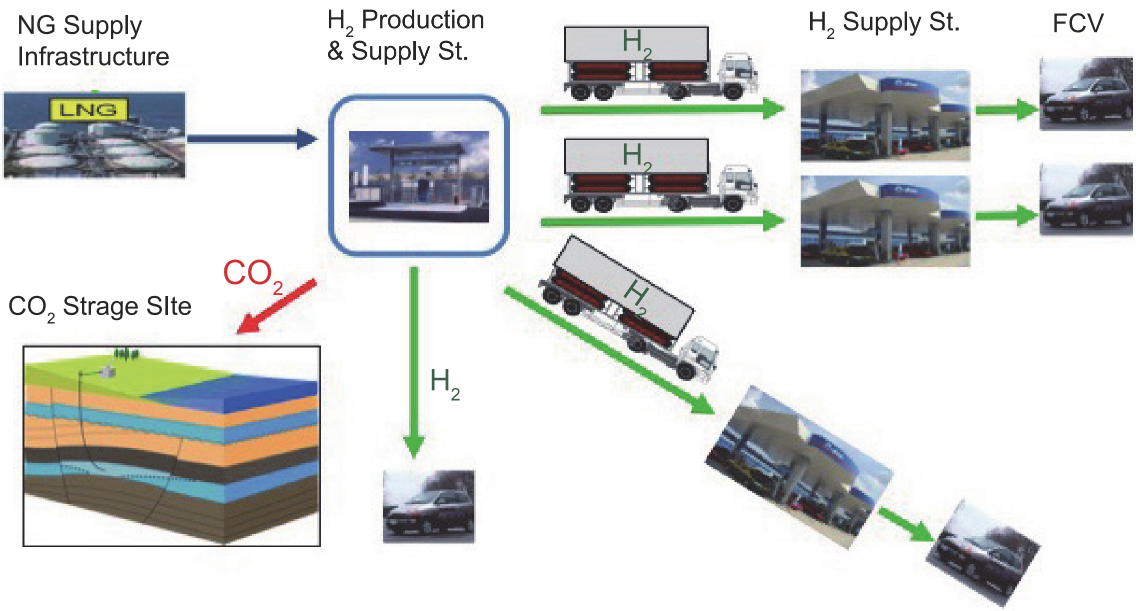

Fig.3 Ideal carbon free Hydrogen supply system with decentralized CCS

The size of CO_2 distribution directly links to obtain PA and permission. We have investigated a new method to monitor and predict the CO_2 behaviour more precise. It is also necessary to introduce some quite new technology to reduce the CO_2 distribution size like as micro bubble method.

Acknowledgements

We gratefully acknowledge the support of the International Institute for Carbon Neutral Energy Research (WPI-I2CNER), sponsored by the Japanese Ministry of Education, Culture, Sports, Science and Technology.

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